

JAN 12 2010

Nalco Docket No. 7774  
Customer No. 49459In the United States Patent and Trademark Office

Applicants:	Brian T. Holland et al.	)	Examiner:	Daniel S. Metzmaier
Serial No.:	10/827,214	)	Art Unit:	1796
Date Filed:	April 19, 2004	)		

For: COLLOIDAL COMPOSITIONS AND METHODS OF PREPARING SAME

Commissioner for Patents  
 P. O. Box 1450  
 Alexandria, VA 22313-1450

**DECLARATION OF PRIOR INVENTION IN THE UNITED STATES OR IN A NAFTA OR  
 WTO MEMBER COUNTRY TO OVERCOME CITED PATENT OR PUBLICATION  
 UNDER 37 C.F.R. § 1.131**

Dear Sir:

This Declaration is to establish completion of the invention in this application in the United States prior to December 5, 2003, the effective date of Cundy et al., "Some observations on the preparation and properties of colloidal silicates. Part I: synthesis of colloidal silicalite-1 and titanasilicalite-1 (TS-1)," Microporous and Mesoporous Materials, 66 (2003): 143 to 156 ("Effective Date of Cundy").

To establish a date of completion of this invention prior to the Effective Date of Cundy, Applicants submit herewith copies of research notebook pages attached as Exhibit A hereto. This exhibit clearly and definitely establishes invention of the subject matter of the currently rejected claims prior to the Effective Date of Cundy.

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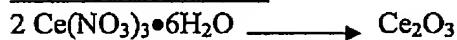
Applicants declare that the document submitted herewith as Exhibit A is dated prior to December 5, 2003. Accordingly, Applicants respectfully assert that this invention was completed prior to the Effective Date of Cundy.

Explanations of the experiments portrayed on pages 1 to 3 of Exhibit A is provided below:

**Notebook Page 3 [Page 1 of Exhibit A]**

**Preparation of Ce<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> co-sol**

Ce(III) stock solution:



$$\frac{\text{Ce}_2\text{O}_3}{2 \text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}} = \frac{328.24}{868.46} = 0.3779$$

For 5%Ce<sub>2</sub>O<sub>3</sub> solution:

$$5/0.3779 = 13.23 \text{ g of cerium nitrate in 100g}$$

Synthesis: Acid sol or silicic acid was prepared by deionizing sodium silicate. The yield was 1.1 kg of acid sol with a specific gravity of 1.042. Silica concentration was calculated using the equation:

$$\% \text{SiO}_2 = \text{Specific gravity} * 163.2207 - 163.1891$$

$$\text{Total silica} = 1.1 * 6.88\% = 75.75 \text{ g}$$

0.75 g CeO<sub>2</sub> is 1%, thus 15g of Ce stock solution was needed.

The acid sol had a 3.05 pH and a 195μS conductance, with the addition of the acidic Ce solution these changed to 2.95 and 980 respectively. This blend was a true solution of ionic Ce(III) and monomeric silicic in an aqueous medium. The complete incorporation of both species in solution is the basis for the homogeneous formation of the corresponding colloidal oxides under the high pH reaction conditions.

- Heel – 200 ml of deionized water and 0.7 g of 45% KOH solution; pH 13.34. Heated to 75°C with steering.

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- Feed – The acid sol/Ce was fed to the heel at 3.66 ml/min once the temperature in the heel reaches 76°C. The pH is monitor; after 1:15 the pH has dropped from the original 11.3 to 7.9. At this time a solution of 0.1N KOH was co-fed to maintain the pH above 7.3. After 4:57 hours both solutions have been added, final pH is 7.3 at 75°C. Heating with stirring continued for 2 hours.
- Concentration – The 2 liter pinkish sol was concentrated to 300 ml by ultra filtration. The filtrate was colorless, indicating that all the Ce was in the colloidal particles

Notebook Pages 17 and 18 [Pages 2 and 3 of Exhibit A]

**Preparation of TiO<sub>2</sub>-SiO<sub>2</sub> co-sol**

**Synthesis:** 1100 g of acid sol was prepared from sodium silicate. Specific gravity was 1.04, corresponding to 6.56% SiO<sub>2</sub>.

$$\text{Total silica} = 1.1\text{kg} * 6.56\% = 72.42\text{g}$$

$$2\% \text{TiO}_2 = 1.44 \text{ g TiO}_2$$

TiO<sub>2</sub> solutions prepared from TiOSO<sub>4</sub> formed a precipitate with time; so it was not practical to store the solutions.

A solution of 3.3g of 87% TiOSO<sub>4</sub>•H<sub>2</sub>O was dissolved in 150 ml of deionized water and was added to the acid sol. This homogeneous metal and silicic acid solution was used as feed for the colloidal particle synthesis.

- Heel – 200 ml of deionized water and 0.7 g of 45% KOH, 12.47 pH at room temperature. Heated with stirring to 77°C.
- Feed – The silica-Ti solution is added to the heel at 3.66 ml/min. After 30 minutes a co-feed of 0.1N KOH started. At the end of the reaction, 41/2 hours, a total of 500 ml KOH were added. The sol was refluxed for one hour
- The dilute sol was milky white and was concentrated by ultra filtration. The excess ions were washed out by dial filtration. Three 1-liter filtrates are collected. Analyses confirmed that the TiO<sub>2</sub> was incorporated into the colloidal particle.

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Ion ppm	SiO <sub>2</sub>	Na	K	SO <sub>4</sub>	Ti
1 <sup>st</sup> filtrate	350	6.4	440	920	7.9
2 <sup>nd</sup> filtrate	200	4.6	300	630	3.2
3 <sup>rd</sup> filtrate	87	2.4	150	340	0.9
Sol			880	190	1,200

The resultant sol was stable for over two years.

**DECLARATION**

As a person signing below, I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated: 1/11/10

Signed:   
Yolanda Ortiz

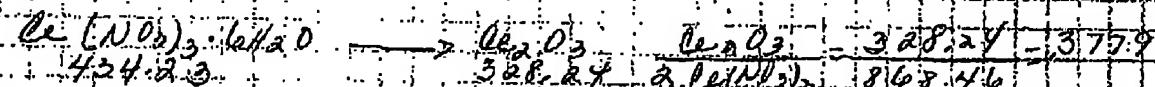
TITLE  $\text{Ce}_2\text{O}_3/\text{SiO}_2$ 

Exhibit A

Page 1 of 3

SUBJECT NO.  
BOOK NO.

3

Preparation of  $\text{Ce}_2\text{O}_3-\text{SiO}_2$  Co-Site

$$\text{5 g of } \text{Ce}_2\text{O}_3 \text{ soln: } 5/377.9 = 13.23 \text{ g of precipitate}$$

$$\text{pH} = 7.12 \quad \text{Ce}_2\text{O}_3 = 1.816 \quad 3.8\text{Ce}(\text{NO}_3)_3 = 0.0069 \text{ meq/g}$$

$$0.434 \times 13.23 = 5.64 \text{ g } \text{NO}_3 \text{ at } 1 \text{ meq/g } / 10 \text{ g of } 5\% \text{ Ce}_2\text{O}_3$$

$$= 0.564 \text{ meq/g}$$

$$75 \text{ ml H}_2\text{O} + 200 \text{ ml DIW} \quad \text{pH } 7.34 \quad T = 19.5$$

$$1.12 \text{ l/kg pH } 7.86 \rightarrow 2.2 \quad \rightarrow 98.0$$

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Exhibit A  
Page 2 of 3

TITLE  $\text{SiO}_2/\text{TiO}_2$   
Co - Sol

PROJECT NO.  
BOOK NO.

17

Reaction with  $\text{TiO}_3\text{SO}_4$

$\Delta S = 11.0 \text{ Jg}$        $C = 2.5 \text{ g/l}$        $pH = 2.32$   
 $\Delta p_{\text{H}} = 1.06$        $\Delta p_{\text{SO}_4} = 5.02$   
 $100 \text{ g } 6.50\% = 73.4 \text{ g } \text{SiO}_2$        $8.2 \text{ g } \text{TiO}_3 = 144 \text{ g } \text{TiO}_3$   
 $\Rightarrow 3.3 \text{ g } \text{TiO}_3 \text{ added to } 100 \text{ g } \text{SiO}_2 \text{ from GES}$        $150 \text{ g } \text{SO}_4^{2-}$   
 added to  $\Delta S \Rightarrow pH = 1.10$        $C = 2.10$        $T = 263 \text{ mg}$

Results  
 $0.79 \text{ L/H}$        $pH = 1.10$        $C = 2.10$   
 $0.90 \text{ L/H}$        $pH = 1.24$        $C = 2.00$

t	vial	pH	C	Notes
0	0	1.05	7.2	3.66 ml/min
10	37	9.55	7.2	
25	72	8.90	7.2	
32	110	7.96	7.3	Addition of 0.1N KOH starts
41	151	7.20	7.3	2.0 ml added
46	241	6.34	7.0	
49	267	5.84	7.3	\$0
55	312	6.2	1.00	Frothing develops
57.0	402	6.8	1.85	
61.3	485	7.12	1.50	2.50 ml added in the first
62.5	551	6.79	1.5	
64.0	559	6.42	1.5	
65.03	621	6.80	1.00	
67.00	878	6.67	1.25	
67.38	1021	6.17	1.50	stop
5.45		6.24		reduced froth here
3.15		7.10	1.7	

Very frothy, no ppt or gel  
 $pH = 6.5$ ,  $C = 1.310$

UV check

3/28 8 liter very slant  
 1st filtrate 350 ml  $pH = 5.60$   $C = 1.350$   
 500 ml added to the cell  
 2nd filtrate 930 ml  $pH = 5.76$   $C = 950$   
 4/15  
 3rd filtrate 710 ml  $pH = 6.15$   $C = 580$

Continued pg 18

SIGNATURE

DATE

HEAD AND UNDERSTOOD BY

DATE

sep [REDACTED] Cheng Slaboski [REDACTED]

18 TITLE

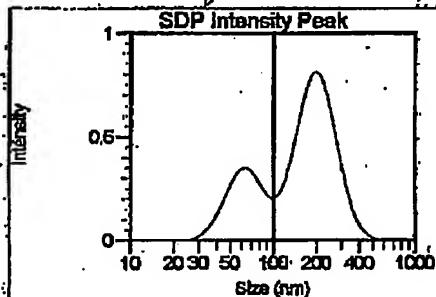
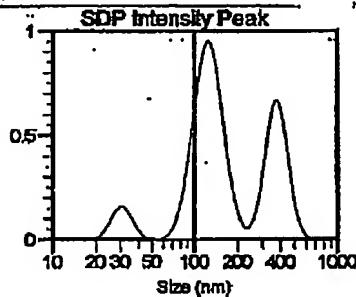
PROJECT NO.  
BOOK NO.

Exhibit A  
Page 3 of 3

Concentrate  
Very thick, translucent. opaque  
300 ml 3.84 g  $\text{C} = 6.55$  set in test tube C  
 $p_1 = 0.53$   $40^\circ\text{C}$  as 18%  
Another test tube collected to  $p_1 = 10.3$  w/v 7.3  
green to opaque 4-5 as 15 B  
After overnight @  $60^\circ\text{C}$  samples look like oil  
but re-disperse when shaken.  
B: remains bath 40-degree, shaking

Q.E.D. date  
11.4.2 ± 49 nm  
spare 0.701

132.3 ± 56.8 mm  
poly 0.701



Amount	Size (nm)	SD (nm)
61.6%	121.5	22.6
31.9%	569.3	49.8
5.5%	12.7	2.1

Amount	Size (nm)	SD (nm)
70.7%	196.4	50.8
29.3%	61.8	15.4

A. Concentrated

B velocity is adjusted

*Amelanchier* Léglise

R & samples with  
thick-walled pores  
& shaking.

	SiO <sub>2</sub>	Na	K	CaO
1st fille	35.0	6.4	4.90	9.20
2nd	30.0	7.6	3.00	4.30
3rd	8.7	2.4	1.50	3.40
Sal melt	diff.		2.0	1.90
Sal ad. iron			2.0	1.8

T-6 Thicker-walled segments  
7-9 (d) shaking

Selmaat dist.  
Selmaat one?

12.00 Z. Patentiel 2.74.9 - 3761  
980. 5-18-61

Stable after 2 years

**SIGNATURE**

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#### **READ AND UNDERSTOOD BY**

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